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Electrical properties of zirconium-modified BiScO$_3$-PbTiO$_3$ piezoelectric ceramics at re-designed phase boundary

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ABSTRACT

Bismuth-based perovskite solid solutions 0.36Bi(Sc$_{1-x}$Zr$_x$)O$_3$-0.64PbTiO$_3$ (BSPT) were designed to obtain morphotropic phase boundary (MPB) between phase tetragonal (T) and rhombohedral (R) to enhance the piezoelectric properties. Their phase structures were investigated by the X-ray diffraction, temperature dependence of dielectric constant. The morphotropic phase boundary separate the rhombohedral and tetragonal phases for the 0.36Bi(Sc$_{1-x}$Zr$_x$)O$_3$-0.64PbTiO$_3$ system at $x = 0.01$. The piezoelectric coefficient d_{33} for the ceramics at $x = 0.01$ is 559 pC/N at 250 °C and 270 pC/N at −100 °C, which is higher than that of traditional piezoelectric materials. Moreover, zirconium doping of 0.36BiScO$_3$-0.64PbTiO$_3$ decreased the coercive field (E_c), dielectric dissipation factor tanδ, and electromechanical coupling factor k_p. Effect of zirconium doping on piezoelectric and electromechanical properties are reported and discussed as a function of temperature. This study indicated the BSPT material at redesigned MPB is a promising candidate for wide temperature range sensor applications.

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1. Introduction

High-temperature piezoelectric sensors are important for deep space exploration, oil drilling and land-based turbine technology [1,2]. PZT ceramics have been investigated for several decades. Different doping strategies had satisfied a wide range of specifications (i.e., high power, high temperature, large response, etc.). Soft PZTs are designed to create a large response (piezoelectric coefficient d_{33} = 750 pC/N for Navy Type IV/PZT 5H) but applications were limited by low Curie temperatures (T_c = 195 °C) and high dielectric losses (loss tangent tanδ = 0.05). Hard PZTs were designed for high power or high-temperature applications, achieving higher Curie temperatures (T_c = 370 °C for Navy Type II/PZT 5A) and lower dielectric losses (tanδ = 0.005); but the piezoelectric displacement is limited (d_{33} = 375 pC/N) [3]. BiFeO$_3$ is one of the piezoelectrics with high Curie temperature of 860 °C, but there are some difficulties in the process of fabricating BiFeO$_3$ ceramics for impurity phase [4–6].

The (1−x)BiScO$_3$-xPbTiO$_3$ materials with a morphotropic phase boundary composition showed a high Curie temperature at 450 °C, which is 100 °C higher than the commercial PZT materials, and a

better piezoelectric property compared to PZT ceramic. BSPT ceramics sparked interest over the last decade for high-temperature piezoelectric actuators due to their high Curie temperature (T_c: 430–450 °C) near the MPB [7–9]. However, these compositions were shown to have greater conductivity and lower electromechanical coupling coefficients [10,11]. The dielectric dissipation factor tanδ of BSPT ceramics is 4% (10^3 Hz), indicating that they may generate too much heat while they work under resonance frequency as power electronic devices. Many attempts have been carried out to improve the electrical properties of BiScO$_3$-based ceramics such as the synthesis of nanosized ceramics and La, Ga doping [12–14]. Mn doping of 0.36BiScO$_3$-0.64PbTiO$_3$ has been reported that can enhance the coercive field (E_c) and high temperature resistivity, and decrease the remanent polarization (P_r), Curie temperature (T_c), dielectric constant (ε_r), loss tangent (tan δ), and piezoelectric coefficient (d_{33}) [15]. Niobium doping does not have any significant effect on piezoelectric properties and decreases the Curie temperature and increases the loss tangent [16]. In this work, we designed a new MPB region of 0.36BiScO$_3$-0.64PbTiO$_3$ by zirconium doping and investigate the effect of donor doping on the dielectric and piezoelectric properties. The donor dopant used in this study is Zr^{4+} substitution for Sc^{3+} on the B site. The influence of zirconium additions on the dielectric and piezoelectric properties are discussed.

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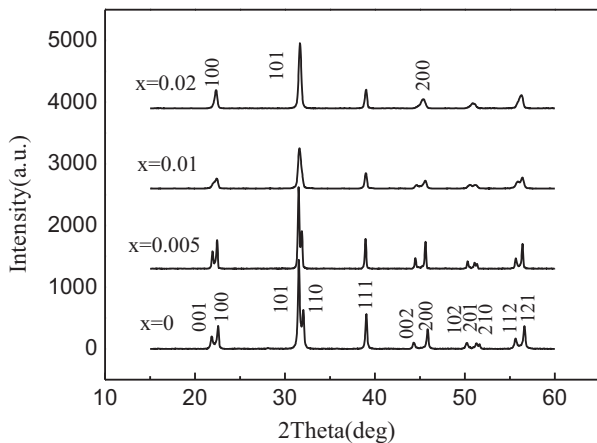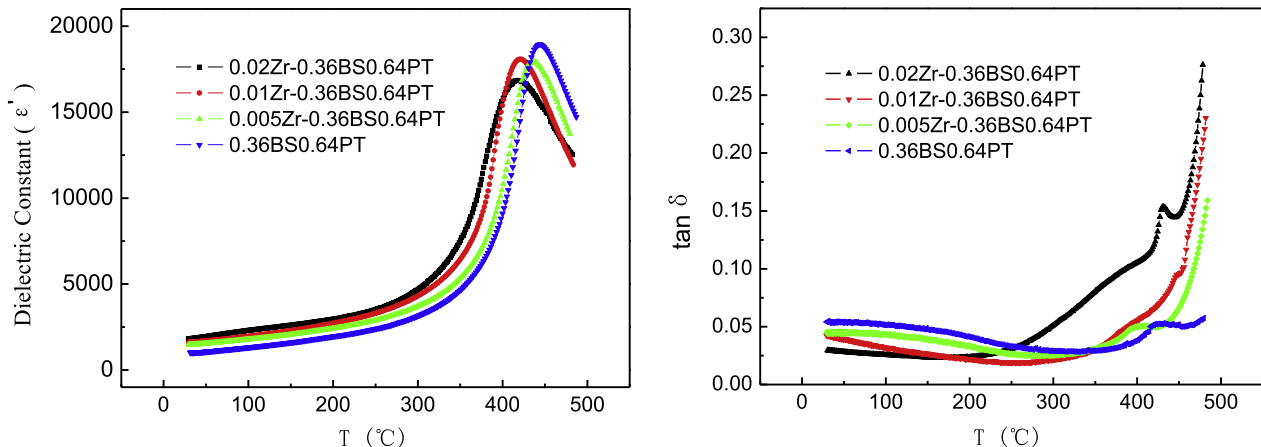E-mail address: zhdai@mail.xjtu.edu.cn (Z. Dai).

2. Experimental

Solid solutions of $0.36Bi(Sc_{1-x}Zr_x)O_3$-$0.64PbTiO_3$ were prepared by the conventional solid-state synthesis. The starting powders were Bi_2O_3 of 99.9% purity, Sc_2O_3 of 99.9% purity, ZrO_2 of 99.9% purity, PbO of 99.9% purity (Kojundo Chemical Laboratory Co., Ltd), and TiO_2 of 99.99% purity (Kojundo Chemical Laboratory Co.,Ltd). Ethanol suspensions of raw materials were vibratory milled with stabilized zirconia media for 24 h, and dried at 90 °C. The dried powders were calcined at 750 °C for 2 h, and a second milling was conducted for 12 h. After drying, 5 wt% PVA was mixed into the powders. Pellets were loosely pressed under uniaxial pressure in an 8 mm die and cold isostatic pressed at 200 MPa. Pressed disks were sintered at 1100 °C for 2 h to attain high densities (96% of theoretical density). Weight loss of pellets was confirmed to be below 4%. The batch formulation accommodated the charge difference on the B site through the formation of A-site vacancies (V_A).

$$0.36(Bi_{1-x/3}, V_{Ax/3})(Sc_{1-x}Zr_x)O_3 - 0.64PbTiO_3 \qquad (1)$$
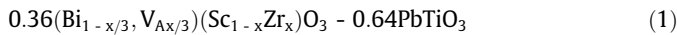
Phase determination for calcined powders and sintered pellets (ground for powder mounts) were made using X-ray diffraction (XRD). For electrical characterization, the sintered pellets were polished to obtain smooth parallel faces. The polished pellets were electroded using a silver paste fired at 700 °C. High temperature dielectric measurements were made using a furnace for temperatures up to 500 °C. Optimally poled samples for piezoelectric mea-

surements were poled in an oil bath under a field of 40 kV/cm at 120 °C for 20 min. Piezoelectric measurements were made on disk samples (8mm diameter and <0.5 mm thick) using a d_{33} meter (Model ZJ-4B, Institute of Acoustics). The temperature dependent electromechanical coupling factor k_p was determined by attaching the poled specimens to a conductive jig placed in a furnace. The bulk density was measured by the Archimedes method.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of different compositions for x = 0, 0.005, 0.01 and 0.02. All peaks were identified as perovskite and no obvious second phases were observed. Typical tetragonal symmetry is observed for the undoped sample for x = 0 and 0.005. As the zirconium content increases, the splitting of the {0 0 1}, {1 1 0} and {0 0 2} peaks becomes weak or disappeared, indicating the decrease of the tetragonality and the existence of mixed phases. The zirconium additions shifted the compositions to the rhombohedral side of the MPB.

The temperature dependences of the dielectric constant and loss for $0.36Bi(Sc_{1-x}Zr_x)O_3$-$0.64PbTiO_3$ ceramics at 1 kHz is presented in Fig. 2. The dielectric constant of the ceramics increases with the increased measured temperature and zirconium doping at temperatures below Curie temperature. At room temperature, the dielectric constant of $0.36BiScO_3$-$0.64PbTiO_3$ (0.36BS-0.64PT) ceramics increased from 1028 to 1791 with 2 mol% zirconium doping. The Curie temperature T_c is determined by the temperature at the dielectric peak. T_c of the $0.36BiScO_3$-$0.64PbTiO_3$ ceramics without zirconium modification is found at around 443 °C, which is consistent with the previous results [1,10]. The T_c values of $0.36Bi(Sc_{1-x}Zr_x)O_3$-$0.64PbTiO_3$ ceramics are 434 °C, 420 °C and 415 °C for zirconium contents of 0.5 mol%, 1 mol% and 2 mol% respectively, which are lower than that of undoped ceramics but higher than that of PZT [17]. Doping with zirconium decreases T_c by a rate of 14 °C/0.01 mol as exhibited by the moving of dielectric constant peak. It has also been noted that there is a general trend of lower transition temperature in ferroelectric perovskites with increasing tolerance factor 't' [3,18]. The concept of a tolerance factor 't' is given in Eq. (2).

$$t = \frac{R_A + R_0}{\sqrt{2}(R_B + R_0)} \qquad (2)$$

where R_A, R_B, and R_o are the ionic radii of A site atom, B site atom and oxygen, respectively. The ionic radius of Sc^{3+} and Zr^{4+} are 0.81 Å and 0.80 Å, respectively. Moreover, our conclusion is consistent with this equation.

Fig. 1. X-ray diffraction patterns of $0.36Bi(Sc_{1-x}Zr_x)O_3$−$0.64PbTiO_3$ with different zirconium contents.

Fig. 2. Dielectric constant ε' and $\tan\delta$ at 1 kHz as a function of temperature for unpoled $0.36Bi(Sc_{1-x}Zr_x)O_3$-$0.64PbTiO_3$ compositions.